Amendments to the Specification

Page 1, please replace the paragraph spanning lines 1-10 below the title with the following rewritten paragraph:

The present invention relates to a process for preparing ~~an aromatic compound~~ metallocenes which is metalated in the ortho position relative to a secondary phosphino group containing two O-P bonds, two N-P bonds or one O-P bond and one N-P bond or a borane adduct thereof by direct replacement of the ortho hydrogen atom by means of an organolithium or organomagnesium compound and, if appropriate, subsequent transmetalation; the ortho-metalated ~~aromatic phosphines~~ metallocene-phosphines which can be obtained by the process; a process for preparing ortho-substituted ~~aromatic phosphines~~ metallocene-phosphines having a secondary phosphine group containing two O-P bonds, two N-P bonds or one O-P bond and one N-P bond by reacting a corresponding ortho-metalated ~~aromatic phosphine~~ metallocene-phosphine with electrophilic compounds; and intermediates obtained in this process.

Page 2, please replace the paragraphs spanning line 34 through page 3, line 23 with the following rewritten paragraphs:

Direct metalation of unactivated hydrogen atoms in the ortho position relative to a P(III) substituent of ~~aromatic compounds~~ metallocenes is not yet known. There is a need for such a synthetic method in order to be able to prepare, in particular, ~~aromatic~~ metallocene 1,2-diphosphines in a simpler manner on a relatively large scale, too.

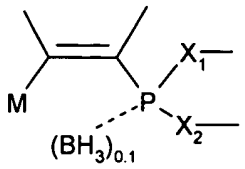
It has now surprisingly been found that the unactivated hydrogen atom in the ortho position relative to the phosphino group in ~~aromatic monophosphines~~ metallocenes can be metalated regioselectively in high yields by means of organic lithium or magnesium compounds when the phosphino group contains amino and/or oxy substituents. The reaction proceeds particularly well when borane of the formula BH_3 is additionally bound to the P atom. These metalated compounds can then be converted by means of many electrophilic compounds with replacement of the metal into valuable intermediates from which, in particular, ligands for homogeneous metal catalysts can be obtained by

converting the phosphine group bearing amino and/or oxy substituents into a secondary phosphine group having hydrocarbon substituents in a manner known per se. Diphosphine ligands and other polydentate ligands having at least one phosphino group ~~and different skeletons~~ can be prepared significantly more economically and in higher total yields even on a relatively large scale by means of this overall process.

In ~~aromatic compounds from the group of~~ metallocenes, for example ferrocenes, metalation generates planar chirality. In addition, it has surprisingly been found that the metalation proceeds highly stereoselectively when the N or O atoms in the phosphino group bear chiral radicals which, in particular, contain a chiral carbon atom in the α position relative to the N or O atoms. In this way, diastereomers are obtained directly in high optical yields by means of the synthesis, so that complicated separation operations are avoidabe.

Page 3, please replace the paragraphs spanning line 25 through page 4, line 18 with the following rewritten paragraphs:

The invention firstly provides a process for preparing ~~aromatic compounds~~ ferrocene, bisindenylferrocene or ruthenocene having a structural element of the formula I in the aromatic hydrocarbon ring,



(I),

where

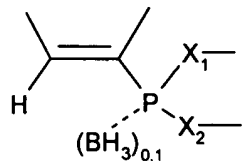
M is -Li, -MgX_3, $(C_1\text{-}C_{18}\text{-alkyl})_3Sn$-, -$ZnX_3$ or -$B(O\text{-}C_1\text{-}C_4\text{-alkyl})_2$,

X_1 and X_2 are each, independently of one another, O or N and C-bonded hydrocarbon or heterohydrocarbon radicals are bound to the free bonds of the O or N atoms,

the group -C=C- together with carbon atoms forms a hydrocarbon aromatic and

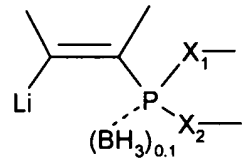
X_3 is Cl, Br or I,

which is characterized in that ~~an aromatic compound~~ ferrocenes, bisindenylferrocenes or ruthenocenes having a structural element of the formula II in the aromatic ring,



(II),

where X_1 and X_2 are as defined above and the group -C=C- together with carbon atoms forms a hydrocarbon aromatic,
is reacted with at least equivalent amounts of alkyllithium, a magnesium Grignard compound or an aliphatic Li sec-amide or X_3Mg sec-amide, and, to prepare compounds of the formula I in which M is $-MgX_3$, $(C_1\text{-}C_{18}\text{-alkyl})_3Sn$-, $-ZnX_3$ or $-B(O\text{-}C_1\text{-}C_4\text{-alkyl})_2$, a lithium compound of the formula Ia,



(Ia),

is reacted with at least equivalent amounts of $Mg(X_3)_2$, $Zn(X_3)_2$, $(C_1\text{-}C_{18}\text{-alkyl})_3SnX_3$ or $B(O\text{-}C_1\text{-}C_4\text{-alkyl})_3$.

~~By way of explanation, structural elements of the formula I can, for the purposes of the invention, be present in various aromatic hydrocarbon rings of an aromatic compound, for example in the two cyclopentadienyl rings of a ferrocene or the aromatic hydrocarbon rings of a fused arene or a biarene.~~

Page 5, please replace the paragraphs spanning line 3-19 with the following rewritten paragraphs:

~~For the purposes of the invention, aromatic hydrocarbons are fused or unfused, aromatic carbocyclic rings, which in the form of either aromatic anionic rings or aromatic rings can be part of a metallocene. They can be, for example, C_6-C_{18}-arenes, preferably C_6-C_{14}-arenes and particularly preferably C_6-C_{10}-arenes which are unsubstituted or substituted by, for example, C_1-C_4-alkyl or C_1-C_4-alkoxy. Aromatic rings can also be fused with aliphatic 5- or 6-membered hydrocarbon rings. Examples of anionic aromatic rings, which are preferably 5-membered, are cyclopentadienyl and indenyl. Specific examples of arenes are benzene, toluene, xylene, cumene, naphthalene, tetralin, naphthacene and fluorene. Examples of possible metallocenes are ferrocene, bisindenylferrocene, ruthenocene and benzenechromium tricarbonyl.~~

In the case of ferrocenes, bisindenylferrocene and ruthenocenes ~~as hydrocarbon aromatic~~, a structural element of the formula I can be present in one cyclopentadienyl ring or in each of the two cyclopentadienyl rings.

Preferred ~~hydrocarbon aromatics are~~ metallocene is ~~benzene, naphthalene and~~ ferrocene.

Page 10, please replace the paragraphs spanning lines 9-20 with the following rewritten paragraphs:

The metalation of ~~aromatics~~ metallocenes involves known reactions which are described, for example, by M. Schlosser (Editor) in Organometallics in Synthesis, John Wiley & Sons (1994) or in Jonathan Clayden Organolithiums: Selectivity for Synthesis (Tetrahedron Organic Chemistry Series), Pergamon Press (2002).

For the purposes of the invention, the expression at least equivalent amounts means the use of from 1 to 1.2 equivalents of a magnesium Grignard compound or an aliphatic Li sec-amide or X_3Mg sec-amide per reactive =CH- group ~~in an aromatic compound~~ of a metallocene, for example from 1 to 1.2 equivalents of $Mg(X_3)_2$, $Zn(X_3)_2$, (C_1-C_{18}-alkyl)$_3SnX_3$ or B(O-C_1-C_4-alkyl)$_3$ per =C-Li group in a compound of the formula Ia.

When ferrocenes having a structural element of the formula II are used, metalation in the second cyclopentadienyl ring can be achieved simultaneously if at least two equivalents of a metalation reagent are used.

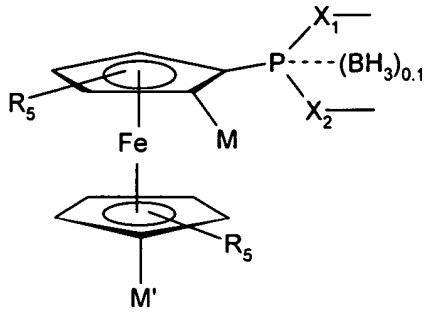
Page 11, please replace the paragraphs spanning lines 4-20 with the following rewritten paragraphs:

Compounds of the formula II are known or can be prepared by methods which are known or analogous to known methods. For example, monolithiated ~~aromatic compounds~~ metallocenes are used as starting materials and are reacted with monohalophosphines of the formula $X_3P(X_1\text{-})X_2\text{-}$, where X_3 is preferably Cl or Br, X_1 and X_2 are O or N and a hydrocarbon radical is bound to the free bonds of X_1- and X_2-. Subsequent to the reaction, the borane BH_3, whose presence is desirable, can be introduced in a manner known per se, for example by reacting the reaction mixture with a borane complex such as $BH_3 \cdot S(CH_3)_2$. Monohalophosphines of the formula $X_3P(X_1\text{-})X_2\text{-}$ are known or can be obtained in a manner known per se from phosphorus trichloride by reaction with alcohols, amines, amino alcohols or diamines.

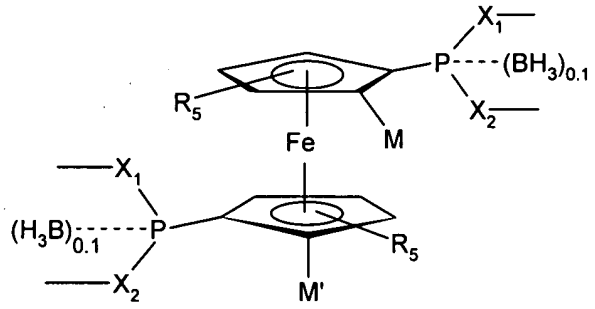
The compounds of the formula I are colored solids which precipitate from the reaction mixture and can be filtered off and then purified if necessary. Storage of the compounds is advantageously carried out in a suspension of the compounds in a medium in which they are not soluble, for example hydrocarbons or ethers (as described above as reaction solvents). The compounds of the formula I can, however, also be reacted further directly after their preparation in their reaction mixture. The compounds of the formula I are valuable intermediates for the preparation of ~~hydrocarbonaromatics~~ metallocenes substituted in the ortho position.

Page 11, please replace the paragraphs spanning line 25 through page 13, line 17 with the following rewritten paragraphs:

In a preferred embodiment, the compounds of the formula I are compounds having a ferrocene skeleton ~~as aromatic compound~~, in particular those corresponding to the formula Ib or Ic,



(Ib),



(Ic),

where

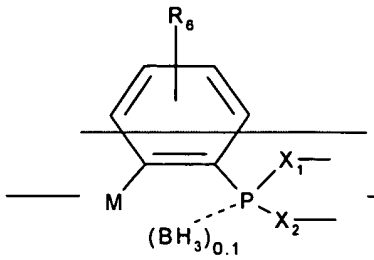
R_5 is C_1-C_4-alkyl and preferably a hydrogen atom,

M is -MgCl, -MgBr and preferably Li,

M' is H, -MgCl, -MgBr or Li and

X_1 and X_2 and also the radicals bound to free bonds of X_1 and X_2 have the abovementioned meanings, including the abovementioned advantageous embodiments and preferences.

~~In another preferred embodiment, the compounds of the formula I are compounds having an arene skeleton as aromatic compound, preferably a benzene or naphthalene skeleton. In particular, they are arenes which correspond to the formula Id,~~



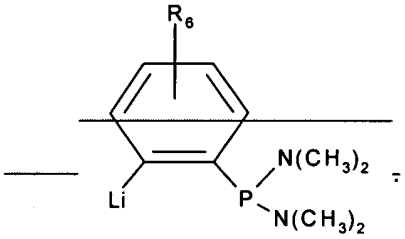
~~(Id),~~

~~where~~

~~R_6 is C_1-C_4-alkyl and preferably a hydrogen atom,~~

~~M is –MgCl, –MgBr and preferably Li and~~

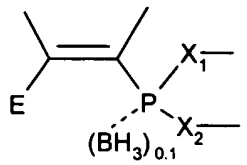
~~X_1 and X_2 and also the radicals bound to free bonds of X_1 and X_2 have the abovementioned meanings, with the exception of ortho-lithiobis(dimethylamino)phosphinobenzene of the formula~~



.

~~In the compounds of the formula Id, the abovementioned advantageous embodiments and preferences apply to X_1 and X_2.~~

The invention also provides a process for preparing ~~aromatic compounds~~ ferrocene, bisindenylferrocene or ruthenocene having a structural element of the formula III in the aromatic ring,



(III),

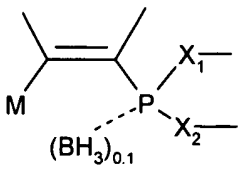
where

X_1 and X_2 and also the radicals bound to free bonds have the abovementioned meanings and

E is the radical of a reactive, electrophilic compound which is able to replace a metal bound to ~~hydrocarbon aromatics~~ ferrocene, bisindenylferrocene or ruthenocene or a bound metal group,

which is characterized in that

a compound having a structural element of the formula I,



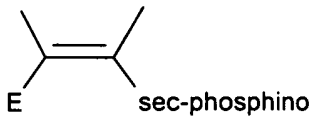
(I),

where

M, X_1 and X_2 and the radicals bound to free bonds have the abovementioned meanings, is reacted with at least equivalent amounts of a reactive electrophilic compound.

Page 20, please replace the paragraph spanning lines 11-25 with the following rewritten paragraph:

Compounds of the formula III having a structural element can be converted in a known manner into ~~hydrocarbon aromatic~~ monophosphines which can be used, for example, as monodentate ligands. Such monophosphines having structural elements of the formula V in one ~~aromatic hydrocarbon ring~~ or ~~in the case of metallocenes~~ also in two aromatic hydrocarbon rings of ferrocene, bisindenylferrocene or ruthenocene,



(V),

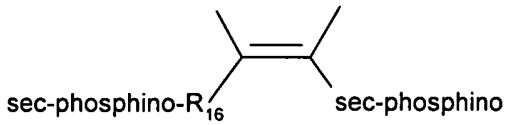
are obtained by

a) removing any borane group present from ~~a compound~~ ferrocene, bisindenylferrocene or ruthenocene having a structural element of the formula III, then splitting off the radicals (hetero)hydrocarbon-X_1, (hetero)hydrocarbon-X_2 or X_1-(hetero)hydrocarbon-X_2 to form a -PCl_2 group or -PBr_2 group and then replacing the Cl or Br atoms by a hydrocarbon radical by means of an organometallic compound (Grignard reagent) to form the sec-phosphino group, or

b) splitting off the radicals (hetero)hydrocarbon-X_1, (hetero)hydrocarbon-X_2 or X_1-(hetero)hydrocarbon-X_2 to form a -PCl_2 group or -PBr_2 group and then replacing the Cl or Br atoms by a hydrocarbon radical by means of an organometallic compound (Grignard reagent) to form the sec-phosphino group and then removing the borane group.

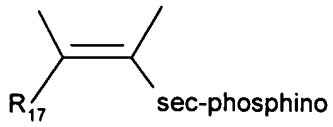
Page 23, please replace the paragraphs spanning line 31 through page 25, line 11 with the following rewritten paragraphs:

The invention further provides a process for preparing hydrocarbon-aromatic diphosphines having structural elements of the formula VI in an ~~aromatic hydrocarbon~~ cyclopentadinyl ring,



(VI),

or having structural elements of the formula VIa in each cyclopentadienyl ring of a ~~metallocene~~ ferrocene, bisindenylferrocene or ruthenocene,



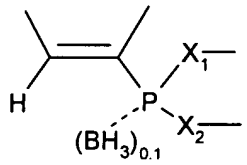
(VIa),

where

R_{16} is a direct bond or a divalent bridging group, with the sec-phosphino in the bridging group being located in the 1, 2 or 3 position relative to the carbon atom of the aromatic ring, and

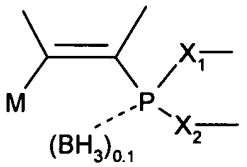
R_{17} is a substituent which is bound via a carbon atom to the cyclopentadienyl ring, which comprises the steps:

a) reaction of ~~an aromatic compound~~ a ferrocene, bisindenylferrocene or ruthenocene having a structural element of the formula II



(II),

with metalation reagents to form ~~an aromatic compound~~ a ferrocene, bisindenylferrocene or ruthenocene having a structural element of the formula I



(I),

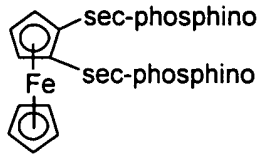
where M, X_1 and X_2 and hydrocarbon radicals bound to the free bonds of the groups X_1 and X_2 have the abovementioned meanings,

b) reaction of the compound of the formula I with an electrophilic and reactive compound, wherein

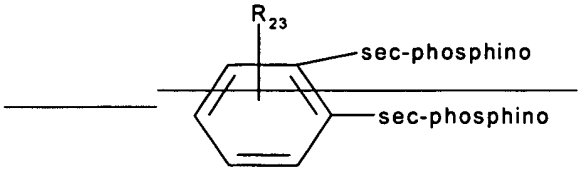
b1) the compound of the formula I is reacted with a sec-phosphine halide to introduce sec-phosphino,
b2) the compound of the formula I is reacted with an electrophilic reactive compound which has a reactive group which can be replaced by sec-phosphino in the 1, 2 or 3 position and the product is subsequently reacted with a metal sec-phosphate or a secondary phosphine to introduce the group -R_{16}-sec-phosphino,
b3) the compound of the formula I is reacted with an electrophilic organic compound which forms an α-carbon atom to introduce the group -R_{17},
c) any borane group present is removed from the compounds obtained in steps b1), b2) or b3) and the radicals (hetero)hydrocarbon-X_1, (hetero)hydrocarbon-X_2 or X_1-(hetero)hydrocarbon-X_2 are subsequently split off to form a -PCl_2 group or -PBr_2 group and the Cl or Br atoms are then replaced by a hydrocarbon radical by means of an organometallic compound (Grignard reagent) to form the sec-phosphino group, or
d) the radicals (hetero)hydrocarbon-X_1, (hetero)hydrocarbon-X_2 or X_1-(hetero)hydrocarbon-X_2 are split off to form a -PCl_2 group or -PBr_2 group and the Cl or Br atoms are then replaced by a hydrocarbon radical by means of an organometallic compound (Grignard reagent) to form the sec-phosphino group and the borane group is then removed.

Page 34, please replace the paragraph spanning line 8 through page 35, line 15 with the following rewritten paragraph:

Diphosphine ligands which have identical or different sec-phosphino groups bound directly to ~~the aromatic skeleton, preferably ferrocenes or benzene~~ ferrocenes, bisindenylferrocenes or ruthenocene, in the 1,2 positions can be prepared in a particularly economical way in few process steps by means of the process of the invention. Another preferred embodiment of the process of the invention is a process for preparing compounds of the formula XII in the form of racemates, diastereomers and pairs of diastereomers ~~and compounds of the formula XIII~~,



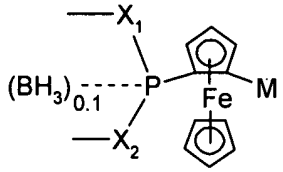
(XII),



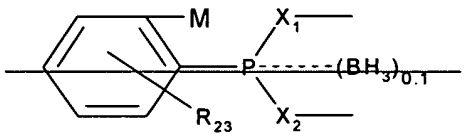
~~(XIII),~~

which comprises the steps

a) reaction of a compound of the formula XIV ~~or XV~~



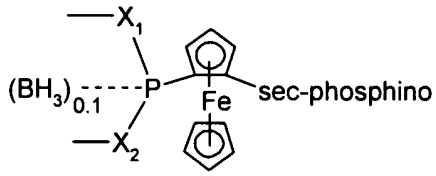
(XIV),



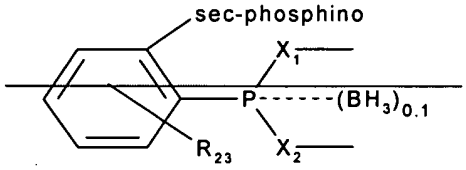
~~(XV),~~

where

M, ~~R_{23}~~ and the group -P(X_1-)(X_2-)----$(BH_3)_{0.1}$ are as defined above, with a sec-phosphine halide (chloride or bromide) to produce compounds of the formula XVI ~~or XVII~~,



(XVI),



~~(XVII),~~

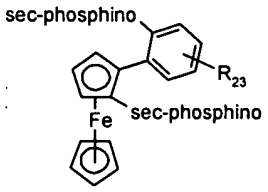
b) preparation of diphosphines of the formulae XII ~~and XIII~~ by

b1) removing any borane group present from a compound of the formula XVI or ~~XVII~~, then splitting off the radicals (hetero)hydrocarbon-X_1, (hetero)hydrocarbon-X_2 or X_1-(hetero)hydrocarbon-X_2 to form a -PCl_2 group or -PBr_2 group and then replacing the Cl or Br atoms by a hydrocarbon radical by means of an organometallic compound (Grignard reagent) to form the sec-phosphino group, or

b2) splitting off the radicals (hetero)hydrocarbon-X_1, (hetero)hydrocarbon-X_2 or X_1-(hetero)hydrocarbon-X_2 to form a -PCl_2 group or -PBr_2 group and then replacing the Cl or Br atoms by a hydrocarbon radical by means of an organometallic compound (Grignard reagent) to form the sec-phosphino group and then removing the borane group.

Page 40, please replace the paragraph spanning line 9 through page 42, line 18 with the following rewritten paragraph:

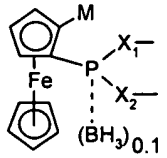
The process of the invention is also particularly useful for preparing ferrocenyldiphosphine ligands, in particular those having different sec-phosphino groups, in which a phosphino group is present in the ortho position of a phenyl substituent of the cyclopentadienyl ring. A further preferred embodiment of the process of the invention is a process for preparing compounds of the formula XXIX in the form of racemates, diastereomers and pairs of diastereomers,



(XXIX),

which comprises the steps

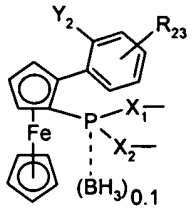
a) reaction of a compound of the formula XX



(XX),

where M is preferably -$Sn(C_1$-C_4-alkyl$)_3$ or -ZnX_3, the group -$P(X_1$-$)(X_2$-$)$----$(BH_3)_{0.1}$ is as defined above,

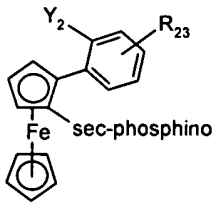
with 1-bromo-2-iodobenzene or 1,2-diiodobenzene in the presence of a Pd catalyst to form a compound of the formula XXX,



(XXX),

where Y_2 is bromine or iodine,

b) to prepare monophosphines of the formula XXXI



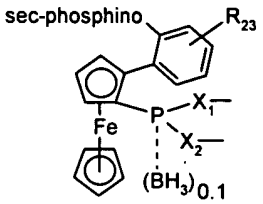
(XXXI),

b1) removing any borane group present from a compound of the formula XXX, then splitting off the radicals (hetero)hydrocarbon-X_1, (hetero)hydrocarbon-X_2 or X_1-(hetero)-hydrocarbon-X_2 to form a -PCl_2 group or -PBr_2 group and then replacing the Cl or Br atoms by a hydrocarbon radical by means of an organometallic compound (Grignard reagent) to form the sec-phosphino group, or

b2) splitting off the radicals ~~hydrocarbon-hydrocarbon~~ (hetero)hydrocarbon-X_1, (hetero)hydrocarbon-X_2 or X_1-(hetero)hydrocarbon-X_2 to form a -PCl_2 group or -PBr_2 group and then replacing the Cl or Br atoms by a hydrocarbon radical by means of an organometallic compound (Grignard reagent) to form the sec-phosphino group and then removing the borane group, and

c) then replacing the bromine or iodine atom by a sec-phosphino group by metalation by means of a lithium alkyl (butyllithium) and subsequent reaction with a sec-phosphine halide, or

d) to prepare compounds of the formula XXXII



(XXXII),

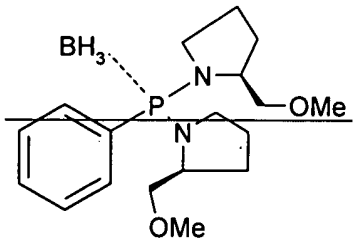
reacting a compound of the formula XX with ortho-sec-phosphinophenyl iodide in the presence of metal halides such as $ZnBr_2$ and Pd catalysts, and

d1) removing any borane group present from a compound of the formula XXXII, then splitting off the radicals (hetero)hydrocarbon-X_1, (hetero)hydrocarbon-X_2 or X_1-(hetero)-hydrocarbon-X_2 to form a -PCl_2 group or -PBr_2 group and then replacing the Cl or Br atoms by a hydrocarbon radical by means of an organometallic compound (Grignard reagent) to form the sec-phosphino group, or

d2) splitting off the radicals (hetero)hydrocarbon-X_1, (hetero)hydrocarbon-X_2 or X_1-(hetero)hydrocarbon-X_2 to form a -PCl_2 group or -PBr_2 group and then replacing the Cl or Br atoms by a hydrocarbon radical by means of an organometallic compound (Grignard reagent) to form the sec-phosphino group and then removing the borane group.

Page 51, please replace the paragraphs spanning line 25 through page 52, line 12 with the following rewritten paragraph:

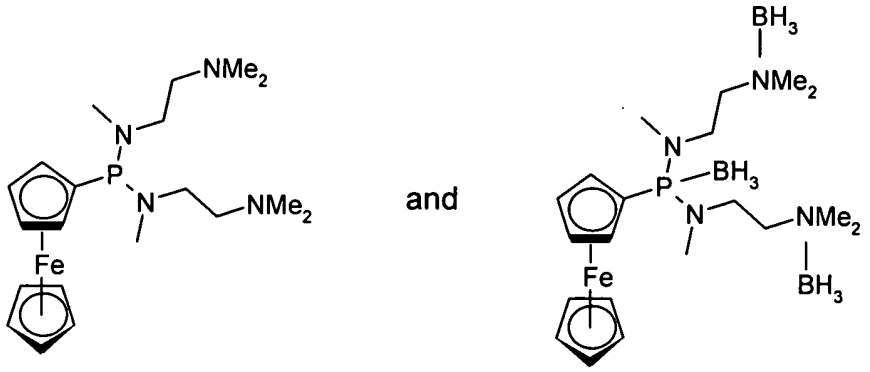
~~Example B4: Preparation of~~



~~In a 250 ml round-bottom flask provided with an argon inlet, $C_6H_5PCl_2$ (1.52 g, 8.47 mmol) is dissolved in dry THF (25 ml) under argon and the solution is cooled to 0°C in an ice bath. $NEthyl_3$ (1.89 g, 18.63 mmol, 2.20 equivalents) is added dropwise and (S)-methoxymethylpyrrolidine (2.00 g, 17.36 mmol, 2.05 equivalents) is then slowly added dropwise. During the addition, the formation of a white precipitate is observed. The ice~~

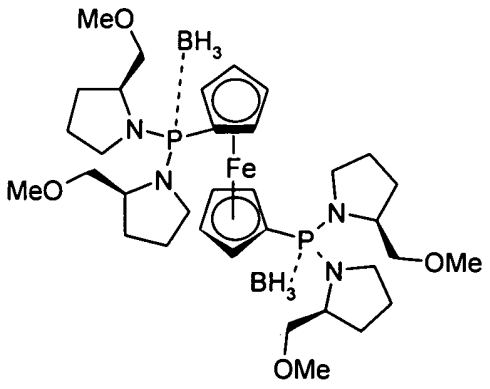
~~bath is removed and the suspension obtained is stirred overnight (14 h) at RT. The white precipitate formed is filtered off under argon by means of a double-ended frit filter and washed with dry THF (2 × 10 ml). BH_3-THF solution (1 M in THF, 10.16 ml, 10.16 mmol, 1.20 equivalents) is subsequently added dropwise and the solution is stirred overnight (14 h) at RT. The reaction mixture is hydrolyzed with saturated NH_4Cl solution (20 ml), TBME (50 ml) is then added, the organic phase is separated off and dried over Na_2SO_4. The solvent is distilled off on a rotary evaporator and the crude product is purified by column chromatography (70 g of silica gel, n-heptane/TBME 3:1). The title compound (1.10 g, 6.66 mmol, 79%) is obtained in the form of a white solid. ^{31}P-NMR (C_6D_6, 121 MHz): 77.9–77.2 (m, br).~~

Example ~~B5~~ B4: Preparation of



Page 53, please replace the paragraph spanning lines 1-18 with the following rewritten paragraph:

Example ~~B6~~ B5:

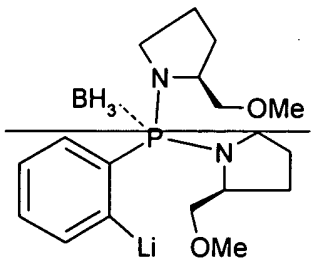


10.95 ml (17.51 mmol) of n-butyllithium (1.6 M in hexane) are added to 2.63 ml (17.51 mmol) of tetramethylethylenediamine (TMEDA) in 2.5 ml of hexane. A solution of 1.32 g (7.1 mmol) of ferrocene in 59 ml of hexane is added dropwise to the resulting solution while stirring and the reaction mixture is stirred further overnight. The resulting orange-brown reaction mixture is subsequently transferred under argon pressure via a cannula into a vessel containing a solution of 18 mmol of the compound of example A1 in 80 ml of THF which has been cooled to 0-5°C. After stirring overnight at RT, an excess of borane-THF complex (50 mmol, 1 M in THF) is added to the reaction mixture. After stirring for 2 hours, the solvent is distilled off under reduced pressure on a rotary evaporator. The residue is taken up in water/TBME and extracted a number of times with TBME (tert-butyl methyl ether). The organic phases are dried over sodium sulfate and evaporated under reduced pressure on a rotary evaporator. Chromatography on silica gel (eluent: heptane/TBME, 3:1) gives 3.9 g of the title compound as a reddish orange oil (yield: 75%). ^{1}H-NMR (C_6D_6, 300 MHz, some characteristic signals): 4.81 (m, 4H, cyclopentadiene), 4.62-4.67 (m, 4H, cyclopentadiene), 3.22 (s, 6H, O-CH_3), 3.12 (s, 6H, O-CH_3).

^{31}P-NMR (C_6D_6, 121 MHz): 79.4 (m, br).

Page 55, please replace the paragraphs spanning lines 3-20 with the following rewritten paragraph:

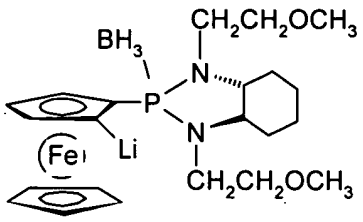
~~Example C2: Preparation of~~



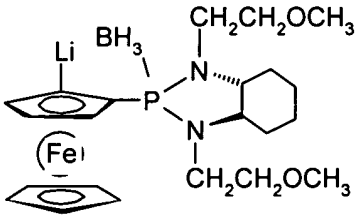
~~In a 50-ml round-bottom flask provided with an argon inlet, the compound of example B4 (200 mg, 0.57 mmol) is dissolved in dry TBME (1.00 ml) and n-hexane (1.00 ml) and the solution obtained is cooled to -78°C. This results in precipitation of the starting material as a white solid. tert-Butyllithium (1.5 M in pentane; 0.38 ml, 0.57 mmol, 1.00~~

~~equivalent) is added dropwise. During this addition, the suspension becomes light yellow. After stirring at -78°C for 30 minutes, the suspension is warmed to RT. The precipitate dissolves to form a yellow solution and after about 5 minutes at RT a white solid precipitates.~~

Example ~~C3~~ C2: Preparation of



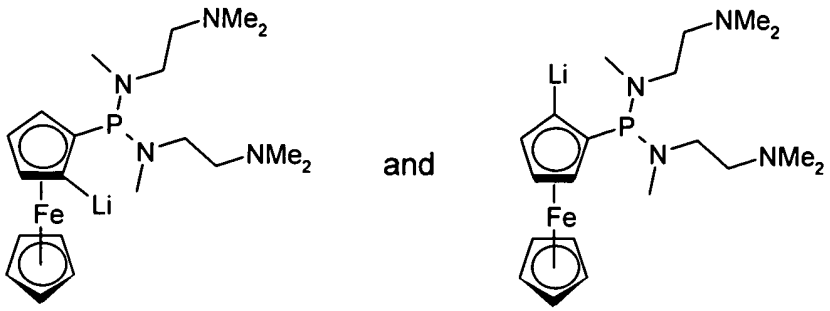
and



459 mg (1.0 mmol) of the compound of example B3 are dissolved in 10 ml of absolute Et_2O. After cooling to -78°C, the starting material partly precipitates and the resulting suspension is reacted with 0.85 ml (1.1 mmol) of a 1.3 M solution of s-butyllithium in cyclohexane:hexane (92:8). During this addition, the orange solid gradually goes into solution, the solution becomes orange-red and after about 30 minutes an orange solid precipitates. One of the two diastereomers is formed preferentially.

Page 56, please replace the paragraph spanning lines 12-18 with the following rewritten paragraph:

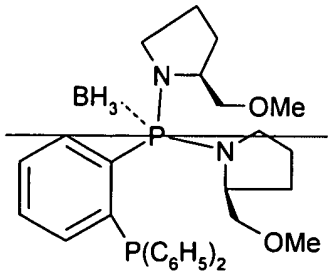
Example ~~C4~~ C3: Preparation of



A solution of 0.14 mmol of the compound of example B5 in 1.0 ml of diethyl ether is cooled to -78°C. This results in the starting material partly precipitating as a light-yellow solid. The suspension is admixed with 0.10 ml (0.14 mmol) of a 1.3 M solution of s-butyllithium in cyclohexane:hexane (92:8). The mixture is subsequently stirred at -25°C for 2 hours. This results in formation of a dark red solution.

Page 59, please replace the paragraphs spanning line 18 through page 60, line 7 with the following rewritten paragraph:

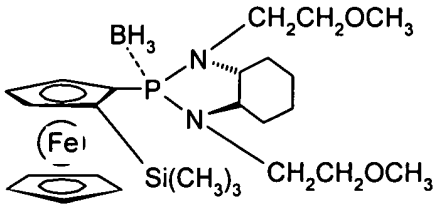
~~Example D5: Preparation of~~



~~In a 50 ml round-bottom flask provided with an argon inlet, the compound of example B4 (200 mg, 0.57 mmol) is dissolved in dry TBME (1.00 ml) and n-hexane (1.00 ml) and the solution obtained is cooled to -78°C. This results in precipitation of the starting material as a white solid. t-Butyllithium (1.5 M in pentane; 0.38 ml, 0.57 mmol, 1.00 equivalent)~~

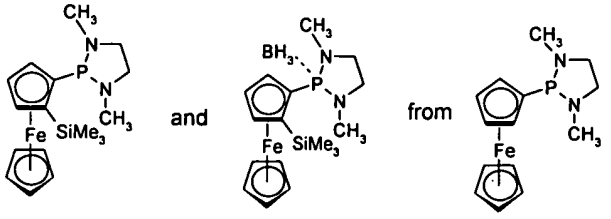
~~is added dropwise. During this addition, the suspension becomes light yellow. After stirring at -78°C for 30 minutes, the suspension is warmed to RT. The precipitate dissolves to form a yellow solution and after about 5 minutes at RT a white solid precipitates (compound of example C2). After stirring at RT for 30 minutes, the solution is cooled back down to -78°C, ClPphenyl$_2$ (151 mg, 0.68 mmol, 1.2 equivalents) is added dropwise, the cooling bath is removed and the suspension is stirred overnight (16 h) while warming to RT. The reaction mixture is hydrolyzed with saturated NH_4Cl solution (10 ml), TBME (20 ml) is added and the organic phase is separated off and dried over Na_2SO_4. The solvent is distilled off on a rotary evaporator and the crude product is purified by column chromatography (50 g of silica gel, n-heptane/TBME 3:1). The title compound (107 mg) is obtained in the form of a yellowish oil which is still contaminated with a little starting compound. ^{31}P NMR (C_6D_6, 121 MHz): 78.0-76.7 (m, br), -13.1 (s).~~

Example ~~D6~~ D5: Preparation of



Page 60, please replace the paragraph spanning lines 18 -21 with the following rewritten paragraph:

Example ~~D7~~ D6: Preparation of

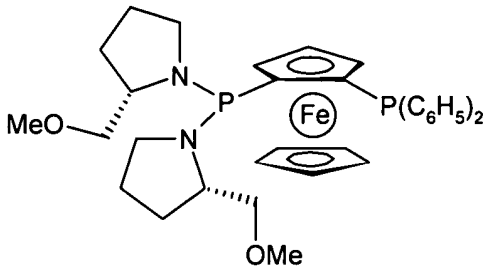


(2) (3) (1)

The starting material (1) is prepared as described in the literature: Nifant'ev I.E., Boricenko A.A., Phosphorus, Sulfur and Silicon 1992, 68, 99.

Page 61, please replace the paragraph spanning lines 18-28 with the following rewritten paragraph:

Example ~~D8~~ D7: Preparation of



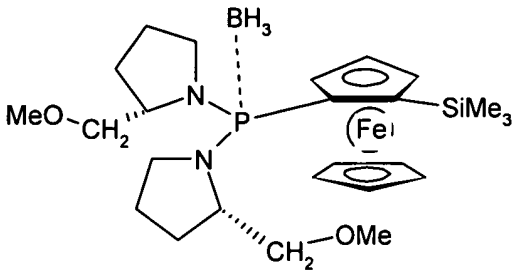
1.2 g (1.87 mmol) of the compound of example D2 are refluxed in 6 ml of diethylamine for 21 hours. Volatile constituents are then removed on a rotary evaporator. The residue is treated 3 times with 2-3 ml each time of diethylamine, refluxed for one hour and the diethylamine is taken off again. 3-5 ml of TBME are subsequently added 3 times to the residue, stirred and the TBME is taken off at 48°C in a high vacuum. The product is obtained virtually quantitatively as an orange oil.

^{31}P-NMR (C_6D_6, 121 MHz): 68.4 (d), -23.5 (d), J_{PP} 73 Hz)

^{1}H-NMR (C_6D_6, 300 MHz, some characteristic signals): 4.114 (s, 5H, cyclopentadiene), 3.114 (s, 3H, O-CH_3), 3.27 (s, 3H, O-CH_3).

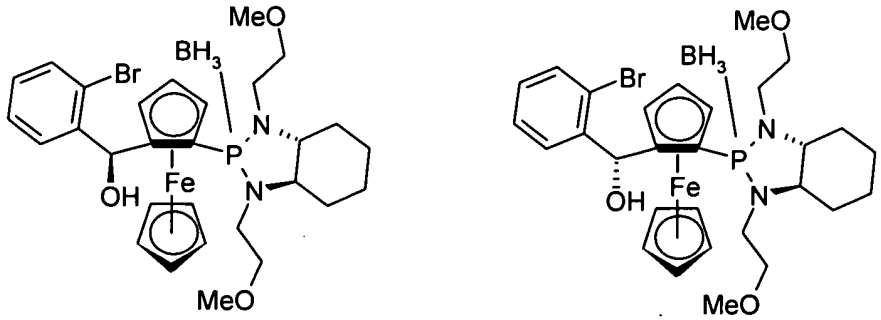
Page 62, please replace the paragraphs spanning line 1 through page 63, line 3 with the rewritten paragraphs:

Example ~~D9~~ D8: Preparation of



1.2 equivalents of a 1.3 M solution of s-butyllithium in cyclohexane:hexane (92:8) are added dropwise to a solution of 0.09 mmol of the compound of example B1 in 1.0 ml of diethyl ether at -78°C. After stirring at -30°C for 2 hours, 1.6 equivalents of trimethylchlorosilane are added. According to NMR, the product comprises 93% of ortho-substituted compound and 7% of starting material. Purification on a silica gel column (eluent: hexane:ethyl acetate (10:1)) gives the title compound as an orange solid. Characteristic NMR signals: ^{1}H-NMR (500 MHz, C_6D_6, 295 K): 0.45 (s, 9H, $Si(CH_3)_3$); 3.07 / 3.29 (each s, 6H, CH_3-O; 4.42 (s, 5H, FcC-H) ppm. $^{31}P\{^1H\}$-NMR (162 MHz, C_6D_6, 295 K): 73.6 (mc) ppm.

Example ~~D10~~ D9: Preparation of:

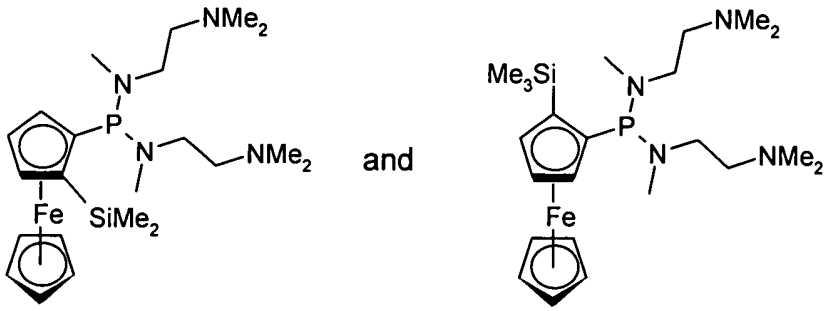


459 mg (1.0 mmol) of the compound of example B3 in 10 ml of absolute Et_2O are reacted with 0.85 ml (1.1 mmol) of a 1.3 M solution of s-butyllithium in cyclohexane:hexane (92:8) at -78°C, the mixture is stirred at 0°C for 2 hours and a solution of 0.14 ml (1.2 mmol) of 2-bromobenzaldehyde in 5 ml of absolute Et_2O is subsequently added dropwise. After warming to RT overnight, the mixture is hydrolyzed with saturated NH_4Cl solution, the phases are separated, the aqueous phase is extracted with

dichloromethane and the combined organic phases are washed with saturated NaCl solution. Drying over $MgSO_4$ and evaporation on a rotary evaporator gives a (73:27) mixture of the diastereomers which can be separated from one another by chromatographic purification on silica gel [eluent: pentane: Et_2O (2:1)]. This gives 314 mg (49%) of one diastereomer and 125 mg (19%) of the other diastereomer as dark orange crystals. Characterization of the main fraction (characteristic NMR signals): ^{1}H-NMR (400 MHz, C_6D_6, 295 K): 3.05 / 3.19 (each s, 6H, CH_3-O); 3.66 (s, 1H, CH-O); 4.39 (s, 5H, FcC-H); 5.98 (s, 1H, OH). $^{13}C\{^1H\}$-NMR (100 MHz, C_6D_6, 295 K): 69.6 (s, 1C, CH-O); 70.6 (s, 5C, FcC-H). $^{31}P\{^1H\}$-NMR (162 MHz, C_6D_6, 295 K): 113.0 (mc) ppm.

Page 63, please replace the paragraph spanning lines 10-19 with the following rewritten paragraph:

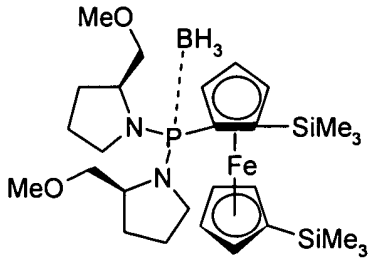
Example ~~D11~~ D10: Preparation of



A solution of 0.14 mmol of the compound of example ~~B5~~ B4 in 1.0 ml of diethyl ether is cooled to -78°C and admixed with 0.10 ml (0.14 mmol) of a 1.3 M solution of s-butyllithium in cyclohexane:hexane (92:8). The mixture is subsequently stirred at -25°C for 2 hours. 32 µl (0.22 mmol) of trimethylchlorosilane are added to the resulting dark red solution and the reaction mixture is stirred at room temperature for one hour. For the purification and characterization, the compound is protected by means of borane. For this purpose, 0.5 mmol of a 10.0 M borane-dimethyl sulfide solution are added. 83% of ortho-substituted compound and 17% of starting material are obtained. Both compounds are protected by borane.

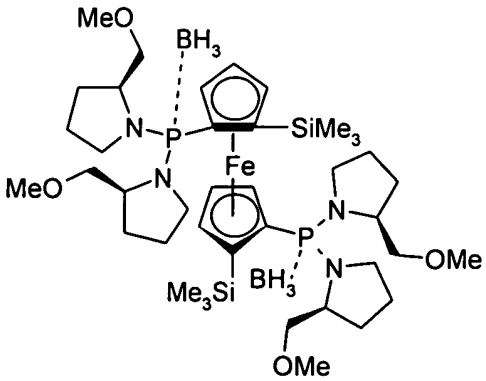
Page 64, please replace the paragraphs spanning line 1 through page 66, line 24 with the following rewritten paragraphs:

Example ~~D12~~ D11: Preparation of



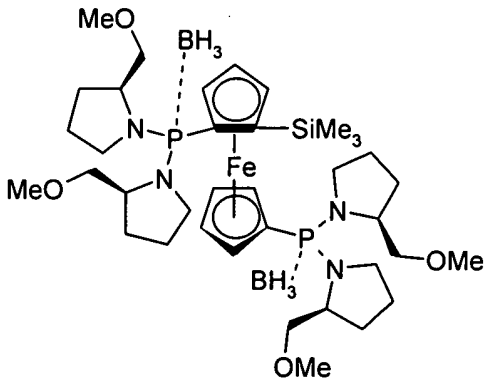
0.77 ml (0.59 mmol) of a 1.3 molar s-butyllithium solution is added dropwise to an orange suspension of 153 mg (0.33 mmol) of the compound B1 in 4 ml of TBME/hexane 1:1 at -30°C. The reaction mixture is stirred at this temperature for 3 hours. During this time, an orange solution is formed first and this then changes back into a suspension. 0.15 ml (1.17 mmol) of chlorotrimethylsilane is subsequently added dropwise at -30°C. The cooling is removed, the reaction mixture is stirred overnight at room temperature and subsequently extracted a number of times in water/TBME. The organic phases are collected, dried over sodium sulfate and evaporated under reduced pressure on a rotary evaporator. Chromatography on silica gel 60 (eluent: heptane/TBME 20:1) gives the title compound in good yield as an orange solid. ^{31}P-NMR (C_6D_6, 121 MHz): 77.9 (m,br). ^{1}H-NMR (C_6D_6, 300 MHz, some characteristic signals): 3.29 (s, 3H, O-CH_3), 3.07 (s, 3H, O-CH_3), 0.49 (s, 9H, $SiMe_3$), 0.26 (s, 9H, $SiMe_3$).

Example ~~D13~~ D12: Preparation of



0.45 ml (0.58 mmol) of a 1.3 molar s-butyllithium solution is added dropwise to an orange solution of 204 mg (0.28 mmol) of the compound of example ~~B6~~ B5 in 4 ml of TBME/hexane 1:1 at -30°C. The reaction mixture is stirred at this temperature for 3 hours. During this time, it becomes red and a small amount of a red substance precipitates. The mixture is subsequently cooled to -40°C and 0.11 ml (0.84 mmol) of chlorotrimethylsilane is added dropwise. The cooling is removed, the reaction mixture is stirred overnight at room temperature and extracted a number of times in water/TBME. The organic phases are collected, dried over sodium sulfate and evaporated under reduced pressure on a rotary evaporator. Chromatography on silica gel 60 (eluent: methylene chloride) gives the title compound in good yield as an orange solid. Characteristic NMR signals: ^{31}P-NMR (C_6D_6, 121 MHz): 78.7 (m,br). ^{1}H-NMR (C_6D_6, 300 MHz, some characteristic signals): 5.86 (m, 2H), 5,08 (m, 2H), 3.33 (s, 6H, O-CH_3), 3.06 (s, 6H, O-CH_3), 0.56 (s, 18H, SiMe3).

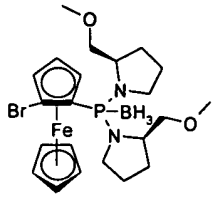
Example ~~D14~~ D13: Preparation of



0.23 ml (0.29 mmol) of a 1.3 molar s-butyllithium solution is added dropwise to an orange solution of 203 mg (0.28 mmol) of the compound of example ~~B6~~ B5 in 4 ml of TBME/hexane 1:1 at -30°C. The reaction mixture is stirred at this temperature for 3 hours. The resulting orange suspension is subsequently cooled to -40°C and 0.22 ml (0.42 mmol) of chlorotrimethylsilane is added dropwise. The cooling is removed, the reaction mixture is stirred overnight at room temperature and subsequently extracted a number of times in water/TBME. The organic phases are combined, dried over sodium sulfate and evaporated under reduced pressure on a rotary evaporator. Chromatography on silica gel 60 (eluent: methylene chloride) gives the title compound in good yield as an

orange, virtually solid oil. ^{31}P-NMR (C_6D_6, 121 MHz): 80.0 (m,br), 77.1 (m,br). ^{1}H-NMR (C_6D_6, 300 MHz, some characteristic signals): 3.35 (s, 3H, O-CH_3), 3.23 (s, 3H, O-CH_3), 3.11 (s, 3H, O-CH_3), 3.05 (s, 3H, O-CH_3), 0.51 (s, 9H, SiMe3).

Example ~~D15~~ D14: Preparation of

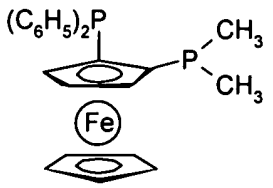


In a 50 ml round-bottom flask provided with an argon inlet, compound B1 (1.00 g, 2.18 mmol) is dissolved in dry TBME (5.00 ml) and n-hexane (5.00 ml) and the solution obtained is cooled to -30°C. This results in precipitation of the starting material as a yellow solid. s-Butyllithium (1.3 M in cyclohexane; 1.76 ml, 2.29 mmol, 1.05 equivalents) is added dropwise. During this addition, the yellow solid gradually goes into solution, the solution becomes orange-red and after about 30 minutes an orange solid precipitates.

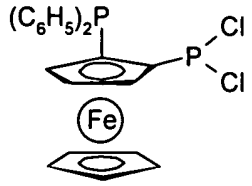
After stirring at -30°C for 2 hours, BrF_2C-CF_2Br (680 mg, 2.62 mmol, 1.2 equivalents) is added dropwise, the cooling bath is removed and the suspension is stirred for 2 hours while warming to RT. The reaction mixture is evaporated to dryness in a high vacuum on a rotary evaporator and used further in step b) without purification. ^{31}P-NMR (C_6D_6, 121 MHz): 76.5 (m).

E) Preparation of diphosphines

Example E1: Preparation of



a) Preparation of



4 equivalents of HCl in the form of a 2 molar HCl/diethyl ether solution are added to a solution of 1.10 g (1.75 mmol) of the compound of example D2 (which has previously been freed of the borane by treatment with diethylamine in a manner analogous to that described in example ~~D8)~~ D7) in 20 ml of TBME at 0°C while stirring, resulting in formation of a precipitate. After stirring at 0°C for a further hour, this precipitate is filtered off under argon and washed a number of times with TBME. The filtrate is evaporated in a high vacuum and the orange product is characterized by means of NMR.
^{31}P-NMR (C_6D_6, 121 MHz): 161.6 (d), -24.6 (d), J_{PP} 170 Hz);
^{1}H-NMR (C_6D_6, 300 MHz, characteristic signals): 3.89 (s, 5H, cyclopentadiene).